Enhancement of orange-yellow electroluminescence extraction from SiN\textsubscript{x} light-emitting devices by silver nanostructures

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Abstract: A multilayer structure of ITO/SiN\textsubscript{x}/Ag/p\textsuperscript{+}-Si/Au was fabricated to improve the extraction of the orange-yellow electroluminescence from SiN\textsubscript{x}-based light-emitting devices (LEDs), and an about 5 times enhancement of external quantum efficiency (EQE) was obtained. This improved light-extraction is mainly originated from the increase of root-mean-square roughness of ITO electrode and reflectivity at longer wavelength via the addition of elongated Ag nanostructures. For the structure with the dipolar resonance peak of Ag nanostructures far from the emission wavelength of SiN\textsubscript{x} matrix, the increased surface roughness of ITO electrode has a dominant effect on the improvement of the light-extraction. Moreover, the decrease of on-series resistance by the addition of Ag nanostructures due to its enhanced local electrical fields also has a benign contribution to the improved EQE. Our work may provide a promising approach to improve the EQE of LEDs, which is not limited to SiN\textsubscript{x} matrix.

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Reference and links


1. Introduction

Despite the enormous efforts that have been made on silicon photonics, the indirect minimum-energy band gap of silicon prevents it from being a preferred material as light sources, which shows poor spontaneous emission efficiency [1–3]. Recently, the hybrid silicon lasers fabricated by bonding a III-V semiconductor laser onto a silicon photonic chip have been achieved by Intel’s Photonics Technology Lab [4]. However, this approach is not fully compatible with current complementary metal-oxide semiconductor (CMOS) techniques. Besides, bonding III-V semiconductor materials onto silicon is very difficult and expensive [4].
Consequently, luminescence materials with cheap and CMOS compatible fabrication process have received lots of attentions in these decades, including silicon nanocrystals [1,5–7], silicon-rich silicon oxide (SiO$_x$) [8–10], silicon-rich silicon nitride (SiN$_x$) [11–13], rare-earth doped silicon-based materials [14–16], and so on. Among these materials, SiN$_x$ film has attracted an extensive research interest in recent years due to its promising luminescence properties [11–13,17,18]. However, the external quantum efficiency (EQE) of SiN$_x$-based light-emitting devices (LEDs) is still too low to satisfy the demands of silicon-based light sources [12,13]. This low EQE is originated from its poor carrier injection and strong nonradiative recombination derived from the band tails and defect states in SiN$_x$ induced by its structural disorder [12,19]. Localized surface plasmons (LSPs, confined excitations of conduction electrons within metal nanostructures) as a novel approach for improving the EQE of LEDs have received a lot of attentions recently, which cannot only improve the carrier injection, but also increase the spontaneous emission rate due to the coupling between LSPs and excitons [18,20–22]. By embedding a silver (Ag) film onto the active matrix, Okamoto et al. [23] achieved a 14 times enhancement of photoluminescence and a 6.8 times increase of internal quantum efficiency from InGaN quantum wells devices. Later, Kwon et al. [21] demonstrated a 32.2% enhancement of light output power from InGaN-based LEDs by inserting Ag nanostructures underneath the luminescence layer via this LSPs-excitons coupling. Lots of researches have attributed the improved luminescence efficiency of LEDs by the addition of metal nanostructures to the coupling between LSPs and excitons in active matrix [20–23]. However, there were still few investigations of other effects via the addition of metal nanostructures on the luminescence performance [18], which would be especially valuable for further improving the EQE of LEDs. For weakening the influence of LSPs-excitons coupling on the improvement of EQE from LEDs, the wavelength of dipolar resonance peak from metal nanostructures should be far from that of the emitted photons, which can be achieved easily by the modulation of the shape and/or size of metal nanostructures [24].

In this letter, we investigate the effect of Ag nanostructures with elongated shapes on the improvement of EQE from SiN$_x$-based LEDs. Ag nanostructures were embedded between the substrate and luminescent matrix by a simple fabrication method. The improvements of electroluminescence (EL) extraction as well as the electrical properties by the addition of Ag nanostructures were investigated.

2. Experimental

A SiN$_x$-based LED with a multilayer structure of ITO/SiN$_x$/Ag/p/p’-Si/Au as shown in Fig. 1(a) was fabricated for the investigation of its EL properties. The substrate was p/p’-Si(100) wafer, where the resistivity and thickness of the epitaxial layer were 0.5 Ω·cm and 17 μm, respectively. After the regular RCA (Radio Corporation of America) cleaning procedure with a final 10% HF solution dipping to remove the surface oxide layer, the substrate was placed into the e-beam evaporation (EBE) chamber immediately for the deposition of Ag layer. The original thickness of Ag layer was ~20 nm (read from a film thickness monitor) with the average deposition rate of ~0.2 Å/s. Denser and smaller sized Ag nanostructures were obtained prior to the following thermal treatment [25]. These smaller sized Ag nanostructures would be coalesced together during the rapid thermal annealing (RTA) process under argon ambient at 500 °C for 60 s due to the Ostwald ripening process [26], and after that the elongated Ag nanostructures could be formed, as shown in Fig. 1(b), where the average radii of longer and shorter axis were ~110 nm and 95 nm (the aspect ratio is ~1.16), respectively. The area root-mean-square (Area RMS) roughness and the average height (Avg. Height) of the Ag nanostructures were about 14.0 nm and 51.8 nm, respectively, measured by an atomic force microscopy (AFM), as shown in Fig. 1(c). After that, SiN$_x$ film with the thickness of ~75 nm was deposited onto the Ag nanostructures by plasma enhanced chemical vapor deposition (PECVD) technical, where nitrogen-diluted 10% silane (SiH$_4$) and ammonia (NH$_3$) were used as the reactant gas sources. The flow rate ratio of SiH$_4$ and NH$_3$, r.f. power, deposition pressure,
and substrate temperature were maintained at 1:1, 6 W, 0.2 Torr, and 300 °C, respectively. To improve the quality and stability of SiN$_x$ film, a RTA process under nitrogen ambient at 400 °C for 120 s was underwent. No stable EL can be detected for the original device without this additional RTA process. After the deposition of SiN$_x$ film, an indium tin oxide (ITO) top circular electrode and a gold metal back contact were both deposited by magnetron sputtering for the fabrication of a SiN$_x$-based LED. Meanwhile, a reference device without Ag nanostructures was fabricated by the same procedure for comparison. For the measurement of extinction spectra, the structure of SiN$_x$/Ag was also fabricated onto a quartz substrate.

The size and shape of Ag nanostructures were characterized by a Hitachi S-4800 scanning electron microscopy (SEM). While an AFM (Dimension Edge, Bruker Ltd., Germany) was employed for the measurement of the surface morphology of the SiN$_x$ films and ITO electrode with and without the addition of Ag nanostructures under the tapping mode. EL signals of SiN$_x$-based LEDs driven by a dc power source were recorded by an Acton SpectraPro-2500i monochromater coupled to a photomultiplier tube (PMT). The extinction and reflectivity spectra were measured by a Hitachi U-4100 spectrophotometer. A Keithley 4200 SCS semiconductor parameter analyzer was employed for the measurement of current-voltage (I-V) characteristics of the devices.

3. Results and discussion

![Image](image_url)

Figure 1(d) represents the extinction spectra of the SiN$_x$ films and the Ag nanostructures with and without the coverage of the SiN$_x$. The dipole resonance peak of Ag nanostructures is located at ~550 nm. As have been investigated, this peak would red-shift gradually with the increase of the aspect ratio [27]. After the coverage of the SiN$_x$ films, this peak is red-shifted to ~780 nm, which is originated from the larger dielectric constant of SiN$_x$ than that of air. A distinct extinction valley at ~500 nm can also be observed, as shown in Fig. 1(d), which may result from the weak parasitic absorption of Ag nanostructures [28]. As have been investigated, this extinction valley may have an instructive contribution to the enhancement of the EL at short wavelength [18]. Obviously, this dipole resonance peak position of Ag nanostructures (~780 nm) is a little far from the emission wavelength of SiN$_x$ matrix (~600 nm) [11,12]. The coupling between LSPs and excitons in SiN$_x$, which can introduce an additional path of...
radiative recombination and enhance the spontaneous emission rate significantly via Purcell effect [23,29], may have little contribution on the improvement of EL efficiency. This little contribution can also be reflected from our early works, where the PL lifetime (τ_{rad}) was decreased only a little from about 1.7 ns for the pristine SiN\textsubscript{x} films to 1.4-1.5 ns for the sample with Ag nanostructures [30]. It means that the increase of the radiative recombination rate (1/τ_{rad}) by the addition of Ag nanostructures was not so much distinct.

Fig. 2. (a) Effects of surface roughening and reflectivity by the addition of Ag nanostructures on light extraction. Atomic force microscopy (AFM) images of the structure surface of (b) Si/SiN\textsubscript{x}; (c) Si/Ag/ SiN\textsubscript{x}; (d) Si/SiN\textsubscript{x}/ITO; and (e) Si/Ag/SiN\textsubscript{x}/ITO.

In our previous investigation, the increase of light extraction efficiency induced by the surface roughening of ITO electrode has a main contribution to the improvement of EQE for the device with Ag nanostructures onto its active matrix [18]. A maximum improvement of 6.5-fold was achieved by the addition of this rough Ag nanostructures layer [18]. For the structure investigated here, where the Ag nanostructures layer is embedded between the substrate and luminescence matrix, two aspects may increase the extraction of light, including the surface roughening of ITO electrode and the increase of reflectivity by the addition of Ag nanostructures, as shown in Fig. 2(a). The surface roughening of ITO electrode can reduce the total reflection of light at the interface between the ITO electrode and the air, labeled as the black solid line arrows in Fig. 2(a), and increase the extraction of light afterward. As shown in Figs. 2(b)-2(e), a significant increase of the Area RMS roughness of the SiN\textsubscript{x} films (from 0.9 nm for the pristine SiN\textsubscript{x} films to 13.2 nm for the sample with Ag) and the ITO electrode (from 1.1 nm for the reference sample to 9.7 nm for the sample with Ag) can be observed by the addition of Ag nanostructures. This increase of the Area RMS roughness is obviously originated from the metal nanostructures layer, whose Area RMS roughness is about 14.0 nm, as shown in Fig. 1(c). Based on the hypothesis that scattering mainly occurs at the regular
reflection direction, a simple model (TIS, total integrated scatter) can be employed to estimate the contribution of this increased RMS roughness on the improvement of light extraction semi-quantitatively by dividing the total power scattered into a hemisphere to the incident power [31]. The value of TIS is proportional to the square of RMS roughness, and an almost 2 orders of magnitude enhancement of light extraction may be achieved by the addition of Ag nanostructures. However, considering the increased nonradiative recombination losses at the rough interface between Ag nanostructures and SiNx matrix due to the scattering at this interface as well as the parasitic absorption loss of Ag nanostructures, this enhancement of light extraction may not be so much distinct. On the other hand, for the structure with Ag nanostructures underneath the SiNx film, the increase of reflectivity can also improve the extraction of light, as shown in Fig. 2(a), labeled as the wide yellow arrows. From the measurement of reflectivity for the devices with and without Ag nanostructures, an obvious increase of reflectivity at longer wavelength can be obtained, as shown in Fig. 3. This increase is induced by the back-scattering by dipolar modes of Ag nanostructures, which is originated from the modification of the angular scattering distribution of the nanostructures by the Si substrate [32]. However, for the Ag nanostructures of this diameter (~200 nm), which is comparable with the order of magnitude of the optical wavelength, the dipolar mode is not so much strong as that for smaller Ag nanostructures [33]. Consequently, this contribution of the increased reflectivity on the improved extraction of light may not be as distinct as that of the increased RMS roughness of ITO electrode. As shown in Fig. 3, an about 2 times enhancement of reflectivity at ~600 nm is achieved by the addition of Ag nanostructures. The reflectivity dip at ~400 nm for the structure of Ag/SiNx might be originated from the interference between the reflected signal from the Ag nanostructures layer and that from the top SiNx layer [34].

For the investigation of this enhanced light extraction on the improvement of EL efficiency of our SiNx-based LEDs, EL spectra of the devices with and without Ag nanostructures were measured, as shown in Fig. 4(a). An obvious enhancement of EL intensity at a same injected current is achieved by the addition of Ag nanostructures. For the reference device, the emission from the SiNx-based LED is very weak. While, this orange-yellow EL can easily be observed by naked eyes even under a lower injected current via the addition of Ag nanostructures, as shown in Fig. 4(b). As have been investigated, this orange-yellow EL is originated from the radiative recombination of the electrons confined in the =Si center and holes located at the valence band tails (composed by the = N tail and Si-Si tail) [12,35]. The full width at half maximum (FWHM) of this orange-yellow EL is about 0.6 eV, which covers the dipolar resonance peak a little. It means that the coupling between the LSPs and excitons might still have an instructive contribution to the improved EL. However, this contribution might be very limited due to the large deviation between the dipolar resonance peak and this emission peak. Obviously, the luminescence intensity is increased significantly and the EL color is gradually blue shifted (from red-orange to orange-yellow) by increasing the injected current, which is consistent with its EL spectra. Meanwhile, the working voltage is decreased significantly by the addition of Ag nanostructures, from 15.9 V to 3.7 V at 10 mA, as shown in Fig. 4(a). Even under a higher injected current (at 50 mA), the working voltage of the device with Ag nanostructures (~6.9 V) is still lower than that for the reference device under a lower injected current (at 10 mA, ~15.9 V). Besides, the stability of the device is also improved by the addition of Ag nanostructures. The reference device is broken out at >12 mA, while for the device with Ag nanostructures, it can still keep working at >60 mA.
Fig. 3. Enhancement factor of reflectivity by dividing the reflectivity intensity of the structure with Ag nanostructures to that of the reference structure, where the reflectivity spectra of them were shown in the inset.

Fig. 4. (a) EL spectra of the SiN₃-based LEDs with and without Ag nanostructures. (b) Charge-coupled device (CCD) pictures for the device with Ag nanostructures under different injected currents. (c) Ratio of the integrated EL intensity to the injected current ($I$) as a function of the input power for the devices with and without Ag nanostructures.

The EQE of EL from a LED is defined as the ratio of the number of photons emitted into the out space per second ($N_{\text{emit}}$) to that of electrons injected into the LED per second ($N_{\text{inj}}$) [31]. The value of $N_{\text{emit}}$ is proportional to the output power of light, which can be characterized by the integrated EL intensities indirectly, and that of $N_{\text{inj}}$ is proportional to the injected current ($I$). Consequently, we can compare the EQE of our SiN₃-based LEDs with and without Ag nanostructures indirectly by comparing their values of integrated EL intensities/$I$ under a same input power or injected current, as shown in Fig. 4(c). On the whole, the EQE of the device with Ag nanostructures is higher than that of the reference device, and an about 5 times enhancement of EQE can be obtained by the addition of Ag nanostructures under ~160 mW. Comparing to the reference device, a higher input power as well as a higher EQE can be achieved for the device with Ag nanostructures. Obviously, this enhancement is not as distinct as been predicted from the calculations of TIS via the changes of RMS roughness of ITO electrode, which may be originated from the nonradiative recombination losses at the rough interface and the parasitic
absorption loss of Ag nanostructures, as have been mentioned above. Interestingly, an efficiency droop phenomenon is occurred in our reference SiNₓ-based LED, as shown in Fig. 4(c), which is improved obviously by the addition of Ag nanostructures. This phenomenon is usually observed in GaN-based LEDs, which may be originated from the carrier overflow and/or Auger recombination [36], and should be investigated further in our SiNₓ luminescence matrix.

As have been observed in Fig. 4(a), the electrical property of SiNₓ-based LEDs is improved significantly by the addition of Ag nanostructures. To investigate the effect of Ag nanostructures on the improvement of electrical properties of our devices in detail, I-V curves of SiNₓ-based LEDs with and without Ag nanostructures are measured, as shown in Fig. 5. An obvious enhancement of carrier injection is achieved via the addition of Ag nanostructures by comparing the injected current of the improved device to that of the reference device under a same applied voltage. To calculate the on-series resistance (Rₛ) of our SiNₓ-based LEDs with and without Ag nanostructures, we rewrite the diode equation \( I = I₀(e^{(V-IRₛ)/nkT}-1) \) to the form of \( I(dV/dI) = IRₛ + nkT/q \), where \( n \) stands for the ideality factor [22,37]. The values of \( Rₛ \) can be obtained from the slope of the linear fittings of \( I(dV/dI) \) vs. \( I \), as shown in the inset of Fig. 5. A distinct decrease of \( Rₛ \) can be achieved by the addition of Ag nanostructures, which contributes to the significantly improved carrier injection and decreased working voltage for the device with Ag, as shown in Figs. 4(a) and 5, respectively. Obviously, this improved electrical property also has an instructive contribution to the enhancement of EQE from SiNₓ-based LEDs. However, this contribution might be not as distinct as that of the increased roughness of the ITO electrode due to the electric field screening effect, where the carriers would be accumulated at the interface states between the contact electrode and the active material and the applied electric field would be screened [38].

Fig. 5. Current-voltage (I-V) curves of the devices with and without Ag nanostructures. Inset is the linear fitting of on-series resistance (Rₛ) for these two devices. The values of \( I \) for the reference device are multiplied by 50 times.
4. Conclusion

The extraction of orange-yellow EL from SiNₓ-based LEDs is improved significantly by the addition of elongated Ag nanostructures, from which an about 5 times enhancement of EQE is achieved. This improved EL extraction is originated from the increase of RMS roughness of ITO electrode and reflectivity at longer wavelength via the introduction of Ag nanostructures. The improvement of electrical properties, especially the decrease of $R_S$ of our devices by the addition of Ag nanostructures, also has an instructive contribution to the increase of EQE from SiNₓ-based LEDs. By carefully modulating the dipolar resonance peak close to the emission wavelength of the SiNₓ-based LEDs, the increased back-scattering originated from the dipolar mode of localized surface plasmons could be further optimized. Besides, the optimization of the RMS roughness of ITO electrode by the modulation of the dimension and morphology of Ag nanostructures might be also an alternative approach for further enhancing the EQE of the SiNₓ-based LEDs. Our results indicate that the introduction of metal nanostructures is a promising approach to improve the luminescence performance of SiNₓ-based LEDs.

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